

## **Amended Set of Claims: #134 - 181**

**Application number: #09/525,176**

**Filing Date: 03/14/2000**

**Inventors: Dr. Savvas Vasileiadis, Ph.D.  
Zivatech**

**Dr. Zoe Ziaka-Vasileiadou, Ph.D.  
Zivatech**

**Date Amendment submitted: March 4, 2004**

134. (currently amended) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for the production of pure hydrogen which includes the use of:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next inner and a most inner one, having the most inner permeable cylinder ~~to be~~ nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the most inner permeable cylinder ~~to be~~ filled with a reforming catalyst in pellet or particle form, and ~~include~~ including gas heating tubes located along the most inner axis for heating the catalyst to the temperature of said reforming reaction, with the catalyst to be in pellet or particle form, with the hydrogen product ~~to be~~ continuously removed via permeation along the most inner membrane, wherein the most inner membrane is made from an inorganic or composite material, with the remaining reaction species ~~to~~ partially ~~permeate~~ permeating as well via the most inner membrane, and with the permeated species ~~to be~~ diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only ~~to be~~ continuously removed via permeation along the next inner membrane and ~~allow for continuous hydrogen withdrawal~~ continuously withdrawn as well out of the most inner catalytic zone and ~~for causing for the~~ continuous equilibrium shift of the reactions evolving within this zone, with next inner membrane ~~to be~~ made from a metal or non-porous inorganic material permeable only to hydrogen, and with the pure hydrogen ~~to permeate~~ permeating through the next inner membrane and withdrawn along the far outer cylindrical zone.

135. (previously presented) The process of claim 134 wherein the most inner membrane is made from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the next inner membrane made from one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

136. (previously presented) The process of claim 134 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas containing methane, landfill gas containing methane, flue gas containing methane, biomass and sewage gas containing methane.

137. (previously presented) The process of claim 134 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a  $\text{CH}_4$  and  $\text{CO}_2$  mixture, acidic natural gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , coal gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , landfill gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , biomass and sewage gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , flue and waste gas mixture containing  $\text{CH}_4$  and  $\text{CO}_2$ .

138. (currently amended) The process of claim 134, ~~with~~ wherein the reject exit stream from the most inner and next inner annular zones is subject to a condensation

step which removes steam from the said reject exit stream, and subsequently passed through a membrane permeator wherein the hydrogen and carbon dioxide gases are separated by permeation via a polymer or composite membrane and the non permeated hydrocarbons, alcohols, and carbon monoxide exit from the non-permeate side of the permeator as a reject stream.

139. (previously presented) The process of claim 138, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reaction zone for additional production of hydrogen and carbon dioxide gas products..

140. (previously presented) The process of claim 138, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is recycled into the initial catalytic most inner reforming zone for continuous reforming reaction.

141. (currently amended) The process of claim 134, ~~with~~ wherein the reject exit stream streams from the most inner and next inner annular zones ~~to~~ have the contained steam removed by condensation and subsequently passed through a cryogenic separator, wherein the contained in stream hydrogen and carbon monoxide are separated as gases, while the hydrocarbons, alcohols, and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding most inner catalytic reforming zone, ~~with~~ wherein the separated hydrogen and carbon

monoxide product mixture coming from the cryogenic separator ~~to be~~ is used in following listed consecutive applications: for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

142. (previously presented) The process of claim 141 wherein the reactant hydrocarbon is methane and the reactant alcohol is methanol.

143. (currently amended) The process of claim 141, wherein a part of the separated liquefied hydrocarbons, alcohols, ~~and/or~~ and carbon dioxide components from the cryogenic separator are mixed with steam and fed into a subsequent reforming reaction zone for additional production of hydrogen and carbon monoxide.

144. (currently amended) The process of claim 134, wherein the reject exit stream consists of hydrogen, carbon monoxide, and unreacted steam and enters as a fuel gas feed into a solid oxide or molten carbonate fuel cell for continuous generation of electricity, ~~with~~ wherein part or all of the permeate hydrogen coming out of the preceding membrane zone ~~to be~~ is fed as well in the fuel cell anode inlet ~~in order to provide~~ providing for the supplementary hydrogen fuel feed.

145. (currently amended) The process of claim 144 wherein the flue hot gas emitted by ~~a~~ the fuel cell is used for at least partial heating of the preceding most inner catalytic reaction zone.

146. (currently amended) The process of claim 144 wherein the flue hot gas emitted by the fuel cell comprises of steam and carbon dioxide and is recycled in the inlet of the preceding most inner catalytic zone for use as a reactant in the reforming reaction.

147. (currently amended) The process of claim 134 wherein the permeate hydrogen from the membrane zone is used as fuel feed in a consecutive fuel cell for continuous generation of electricity, with wherein the fuel cell ~~to-be~~ is one of the listed types: solid oxide, molten carbonate, proton exchange membrane, phosphoric acid, alkaline.

148. (currently amended) The process of claim 147 wherein the flue hot gas emitted by the fuel cell ~~to-be~~ is used for at least partial heating of the preceding most inner catalytic zone.

149. (currently amended) The process of claim 147 wherein the flue hot gas, emitted by the solid oxide and molten carbonate fuel cell, which contains steam and carbon dioxide, ~~to-be~~ is recycled in the inlet of the preceding most inner catalytic zone for use as a reactant in the reforming reaction.

150. (currently amended) The process of claim 147, wherein the fuel cell is of a cylindrical shape and its fuel anode encloses the cylindrical permreactor ~~in order to receive and consume~~ by receiving and consuming directly the permeate hydrogen gas as

fuel, ~~and with~~ wherein the flue hot gas emitted by the fuel cell ~~to be~~ is used for at least partial heating of the enclosed most inner catalytic reforming zone.

151. (previously presented) The process of claim 134, wherein the reject exit stream rich in hydrogen and carbon monoxide after steam condensation is used as fuel feed in a gas engine or a gas turbine for continuous generation of electricity, with wherein part or all of the permeate hydrogen coming out of the preceding membrane zone ~~to be~~ is fed as well in the engine or turbine ~~in order to provide~~ providing for the supplementary hydrogen fuel.

152. (currently amended) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for production of pure hydrogen which includes the use of:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder ~~to be~~ nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders ~~to be~~ filled with a reforming catalyst in pellet or particle form, ~~with the catalyst to be in pellet or particle form~~, with hydrogen ~~to be~~ continuously removed via permeation along the next-inner membrane wherein ~~the~~ next-inner membrane is made from an inorganic or composite material, with the remaining reaction species ~~to~~ partially permeate permeating as well via the next inner membrane, ~~and~~ with the permeated species ~~to be~~ diluted by an inert

carrier gas flowing along the next inner annular zone, with hydrogen only ~~to be~~ continuously removed via permeation along the most inner membrane ~~in order to allow~~ allowing as well for the continuous ~~hydrogen~~ withdrawal of hydrogen out of the far outer catalytic zone and for the continuous equilibrium shift of the reactions evolving within this zone, with the said most inner membrane ~~to be~~ made from a metal or non-porous inorganic material, and with the ~~permeate~~ permeated pure hydrogen ~~to~~ withdrawn along the most inner cylindrical zone.

153. (previously presented) The process of claim 152 wherein the next inner membrane is made from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made from one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

154. (previously presented) The process of claim 152 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas containing methane, landfill gas containing methane, flue or waste gas containing methane, biomass and sewage gas containing methane.



155. (previously presented) The process of claim 152 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a  $\text{CH}_4$  and  $\text{CO}_2$  mixture, acidic natural gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , coal gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , landfill gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , biomass and sewage gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , flue and waste gas mixture containing  $\text{CH}_4$  and  $\text{CO}_2$ .

156. (currently amended) The process of claim 152, wherein the reject exit ~~stream~~ streams from the far outer and next inner annular zones ~~to~~ have the contained steam removed by condensation, and subsequently ~~be~~ passed through a membrane permeator, wherein the contained in stream hydrogen and carbon dioxide are separated by permeation via a polymer or composite membrane and the non permeated hydrocarbons, alcohols, and carbon monoxide exit from the non-permeate side of the permeator as a reject stream, ~~with~~ wherein the separated hydrogen and carbon dioxide product mixture ~~to-be~~ is used as a combined fuel-oxidant feed in a molten carbonate fuel cell.

157. (previously presented) The process of claim 156, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reaction zone for additional production of hydrogen and carbon dioxide gas products.

158. (previously presented) The process of claim 156, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols,

and carbon monoxide is recycled into the preceding catalytic far outer reforming zone for continuous reforming reaction.

159. (currently amended) The process of claim 152, wherein the reject exit stream ~~streams~~ from the far outer and next inner annular zones ~~to~~ have the contained steam removed by condensation and subsequently passed through a cryogenic separator wherein the contained in stream hydrogen and carbon monoxide are separated as gases while the hydrocarbons, alcohols, and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding far outer catalytic reforming zone, with wherein the separated hydrogen and carbon monoxide product mixture coming from the cryogenic separator ~~to be~~ is used in the following listed consecutive applications: for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

160. (previously presented) The process of claim 159 wherein the reactant hydrocarbon is methane and the reactant alcohol is methanol.

161. (currently amended) The process of claim 159, wherein ~~a~~ part of the separated liquefied hydrocarbons, alcohols, and carbon dioxide components from the cryogenic separator ~~are~~ is mixed with steam and fed into a consecutive reforming reaction zone for additional production of hydrogen and carbon monoxide which is used in the following listed consecutive applications: for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

162. (currently amended) The process of claim 152, wherein the reject exit stream consists of hydrogen, carbon monoxide, and unreacted steam ~~which~~ and enters as a fuel gas feed into a solid oxide or molten carbonate fuel cell for continuous generation of electricity, ~~with~~ wherein part or all of the permeate hydrogen coming out of the preceding membrane zone ~~to-be~~ is fed as well in the fuel cell anode inlet ~~in order to~~ providing for supplementary hydrogen fuel feed.

163. (currently amended) The process of claim 162 wherein the flue hot gas emitted by the fuel cell ~~to-be~~ is used for at least partial heating of the preceding far outer catalytic reaction zone.

164. (currently amended) The process of claim 162 wherein the flue hot gas emitted by the fuel cell containing steam and carbon dioxide, ~~to-be~~ is recycled in the inlet of the preceding far outer catalytic zone for use as a reactant in the reforming reaction.

165. (currently amended) The process of claim 152 wherein the permeate hydrogen from the membrane zone is used as fuel feed in a consecutive fuel cell for continuous generation of electricity, with wherein the fuel cell ~~to-be~~ is one of the listed types: solid oxide, molten carbonate, proton exchange membrane, phosphoric acid, alkaline.

166. ( currently amended ) The process of claim 165 wherein the flue hot gas emitted by the fuel cell ~~to be is~~ is used for at least partial heating of the preceding far outer catalytic zone.

167. (currently amended) The process of claim 165 wherein the flue hot gas containing steam and carbon dioxide, emitted by the solid oxide and molten carbonate fuel cell, ~~to be is~~ is recycled in the inlet of the preceding far outer catalytic zone for use as a reactant in the reforming reaction.

168. (currently amended) The process of claim 165, wherein the fuel cell is of ~~a~~ cylindrical shape and its fuel anode encloses the cylindrical permreactor ~~in order to receive and consume~~ by receiving and consuming directly the permeate hydrogen gas as fuel, ~~and with wherein~~ wherein the flue hot gas emitted by the fuel cell ~~to be is~~ is used for at least partial heating of the enclosed far outer catalytic reforming zone.

169. (currently amended ) The process of claim 152, wherein the reject exit stream rich in hydrogen and carbon monoxide after steam condensation is used as fuel feed in a gas engine or a gas turbine for continuous generation of electricity, ~~with wherein~~ wherein part or all of the permeate hydrogen coming out of the preceding membrane zone ~~to be is~~ is fed as well in the engine or turbine ~~in order to provide~~ providing for the supplementary hydrogen fuel.

170. (currently amended) A process for conducting catalytic hydrocarbon reforming with carbon dioxide, for production of pure hydrogen and carbon dioxide which includes the use of:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder ~~to be~~ nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders ~~to be~~ filled with a reforming catalyst in pellet or particle form, with hydrogen and carbon dioxide ~~to be~~ continuously removed via permeation along the next-inner membrane wherein ~~the~~ next-inner membrane is made from an inorganic or composite material, with the remaining reaction species ~~to~~ partially permeate permeating as well via the next inner membrane and with the permeated species ~~to be~~ diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen and carbon dioxide species ~~to be~~ continuously removed via permeation along the most inner membrane, with the most inner membrane ~~to be~~ made from a polymer or inorganic material which is permeable to both hydrogen and carbon dioxide species, with the permeated said binary hydrogen-carbon dioxide mixture ~~to be~~ withdrawn by flowing along the most inner cylindrical zone.

171. (new) The process of claim 170 wherein the next inner membrane is made from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made from one or more materials selected

from the group consisting of alumina, silica, titania, zirconia, yttria, polyimides, polycarbonates, polybenzimidazoles, polyphosphazenes, polysulfones.

172. (previously presented) The process of claim 170 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas containing methane, landfill gas containing methane, flue and waste gas containing methane, biomass and sewage gas containing methane.

173. (previously presented) The process of claim 170 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a  $\text{CH}_4$  and  $\text{CO}_2$  mixture, acidic natural gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , coal gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , landfill gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , biomass and sewage gas containing  $\text{CH}_4$  and  $\text{CO}_2$ , flue and waste gas mixtures containing  $\text{CH}_4$  and  $\text{CO}_2$ .

174. (currently amended) The process of claim 170 wherein the combined permeate from the membrane, hydrogen and carbon dioxide gas mixture is consumed as fuel-oxidant in a consecutive molten carbonate fuel cell.

175. (currently amended) The process of claim 174 wherein the flue hot gas emitted by the molten carbonate fuel cell ~~to be~~ is used for at least partial heating of the preceding far outer catalytic reaction zone.

176. (currently amended) The process of claim 174 wherein flue hot gas emitted by the molten carbonate fuel cell containing carbon dioxide, ~~to be~~ is recycled in the inlet of the preceding far outer catalytic zone for use as reactant in the reforming reaction.

177. (currently amended) The process of claim 174, wherein the molten carbonate fuel cell is of ~~a~~ cylindrical shape and its fuel anode encloses the cylindrical permreactor ~~in order to receive and consume~~ by receiving and consuming directly as fuel the permeate hydrogen-carbon dioxide mixture, ~~and with~~ wherein the flue hot gas emitted by the fuel cell ~~to be~~ is used for at least partial heating of the enclosed far outer catalytic reforming zone.

178. (previously presented) The process of claim 170 wherein the reject exit stream consisting of hydrogen and carbon monoxide enters as fuel gas feed in the anode of a consecutive solid oxide or molten carbonate fuel cell for continuous generation of electricity.

179. (currently amended) The process of claim 178 ~~with~~ wherein the flue hot gas emitted by the solid oxide or molten carbonate fuel cell ~~to be~~ is used for at least partial heating of the preceding far outer catalytic zone.

180. ( currently amended ) The process of claim 178 ~~with~~ wherein the flue hot gas emitted by the solid oxide or molten carbonate fuel cell containing carbon dioxide, ~~to be~~ is recycled in the inlet of the preceding far outer catalytic zone for use as reactant in the reforming reaction.

181. ( currently amended ) The process of claim 170, wherein the reject exit stream rich in hydrogen and carbon monoxide after steam condensation is used as fuel fed in a gas engine or a gas turbine for continuous generation of electricity, ~~with~~ wherein part or all of the permeate hydrogen and carbon dioxide coming out of the preceding membrane zone ~~to be~~ is fed as well in the engine or turbine in order to provide for supplementary hydrogen fuel.